

In the event, heating of 7-Co<sub>2</sub>(CO)<sub>6</sub> in heptane at 110 °C (sealed tube) gives 51% of an 88:12 ratio of enones. The products have readily resolved proton NMR resonances at  $\delta$  5.76 (major isomer) and  $\delta$  5.89 (minor isomer), respectively, but no information concerning the stereochemistry of the major product could be inferred at this point. Reduction (Li/NH<sub>3</sub>, 89%) gives a mixture of saturated ketones 8 whose major constituent clearly possesses the desired configuration at C-9, based on superimposability of its NMR signals with those of the minor constituent in spectra obtained by Piers for a 42:58 mixture of isomers of 8. Completion of the synthesis of pentalenene was achieved by following the published procedure; spectroscopic data for the product were identical in all respects with that of authentic  $(\pm)$ -pentalenene.<sup>11,12</sup>

The interactions associated with the intramolecular Pauson-Khand reaction are more than sufficient to give rise to usable stereoselectivity in relatively complex situations. The interaction above is not obviously greater than those that give rise to rather modest regioselectivities in some intermolecular versions of the reaction.<sup>13,14</sup> The difference in transition state energy between endo and exo C-9 methyl leading to the intermediate shown is about 1 kcal/mol. Apparently the transition state associated with alkene insertion in the intramolecular process is more product-like, consistent with the high stereoselectivities found by Magnus in Pauson-Khand syntheses of substituted bicyclic systems.<sup>15</sup> It was necessary in the latter cases to generate the controlling interaction by attachment of a bulky group to the alkyne terminus. In our system this is unnecessary, as the control elements are already present in the framework of the incipient tricyclic itself.

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## [n]Staffanes: A Molecular-Size "Tinkertoy"<sup>1</sup> Construction Set for Nanotechnology. Preparation of End-Functionalized Telomers and a Polymer of [1.1.1]Propellane

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Nanotechnology,<sup>2</sup> custom design and construction of molecular-size mechanical structures, has been a subject of speculation for some time.3 We have telomerized and polymerized [1.1.1] propellane (1) and obtained a family of end-functionalized inert, insulating, transparent, and straight beams with a van der Waals radius of 2.3 Å and a length increment of 3.35 Å for use as construction elements. We propose the trivial name [n] staffanes for the parent hydrocarbons.<sup>4</sup> Presently, we describe a one-step synthesis of singly functionalized telomers [n]2, with emphasis on the esters [n]2a and the acids [n]2b, including a low molecular weight polymer [poly]2a. A one-step preparation of doubly end-functionalized telomers of 1 will be reported separately.<sup>4</sup>

Previously described molecules of this type were the formal telomers [n]3 of [2.2.2] propellane, originated by Zimmerman,<sup>6</sup> known up to n = 2, and used as spacers in studies of energy<sup>6</sup> and electron<sup>7</sup> transfer. Unlike the synthesis of  $[n]_2$ , the preparation of the higher members of this series is laborious.

[1.1.1]Propellane<sup>8</sup> (1) is readily accessible from methallyl dichloride.<sup>9</sup> The formation of telomer side-products up to n =3 during radical addition of cyanogen bromide to 1 has been detected,<sup>10</sup> and very recently a low-molecular weight polymer was obtained from a related monomer, 2,4-trimethylene-1, by anionic polymerization.11

We have detected the formation of numerous telomers under radical addition conditions, [n]2a - [n]2i, n = 1-4 or 5, and isolated many of them in pure state. Their relative amounts depend on the choice of reactant concentrations. Chlorocarbonylation of [n]2a, n = 2, 3, yielded derivatives of [n]2j. Some of the attempted telomerization reactions did not proceed smoothly; e.g., the reaction of PhCH<sub>2</sub>Br with 1 yielded some [2]2k and bibenzyl in addition to [1]2l.

Efficient preparation of [n]2a requires ether-free solutions of 1, obtained in a 15% yield based on methallyl dichloride by substituting TMEDA for ether in the Szeimies synthesis. In a typical procedure, a 1.4 M solution of 1 in pentane (65 mL) reacted with methyl formate (800 mL) upon irradiation in the presence of benzoyl peroxide (0.4 g). The individual telomers [n]2awere separated by crystallization of the acids and potassium salts and by sublimation. On the basis of methallyl dichloride, the overall three-step yields of purified materials were about 3% for n = 1, 2, about 1.5% for n = 3, 4, and about 0.8% for n = 5, with about 3% of 1 accounted for as higher molecular weight material. It is possible to find reaction conditions under which only the

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<sup>(11)</sup> We are extremely grateful to Prof. Edward Piers of the University of British Columbia for providing us with details of his conversion of 8 into 1 and for supplying IR and NMR spectra of these compounds for comparison purposes.

<sup>(12)</sup> Satisfactory spectroscopic data for all compounds (300 MHz <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR) and satisfactory elemental analyses for compounds **5** and 6 were obtained.

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<sup>(1)</sup> Tinkertoy is a trade-mark of the Questor Education Products Company, used to designate a children's toy construction set consisting of straight beams and connectors.

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Melting points of (i) [n]2b, (ii) [n]2a, (iii) fatty acids Figure 1.  $C_nH_{2n+1}COOH$ , and (iv) their methyl esters. Horizontal scales give n and chain length. The upper one applies to (i) and (ii), the lower one to (iii) and (iv).

monomer (n = 1) is formed.<sup>12</sup> At low concentrations of methyl formate and also under anionic polymerization conditions (nbutyllithium, 2-25%), practically only [poly]2 is obtained (unoptimized yield,  $\sim 50\%$ ).



The telomers  $[n]^2$  have strikingly high melting points (Figure 1) and remarkable thermal stability up to about 300 °C, considering their high-energy content (the strain energy of bicyclo-[1.1.1]pentane is 68 kcal/mol<sup>13</sup>). Differential scanning calorimetry on a sealed sample of [4]2a shows a decomposition exotherm at ~320 °C (145.7 kcal/mol). [poly]2a decomposes violently at 290 °C with an  $\sim 80\%$  weight loss. In keeping with the high melting points, the solubility of the higher telomers is poor, and no solvent for [poly]2a was found. Its X-ray diffraction pattern shows a high degree of crystallinity. Its solubility is increased dramatically upon extensive chlorination,14 and this clearly points the way toward improvements in the solubility of all the telomers.

X-ray structure analysis<sup>15</sup> on [2]2a (Figure 2) and [2]2k yields an inter-ring C-C bond length of only  $\sim 1.48$  Å, in keeping with expectations,<sup>16</sup> and a bridgehead-bridgehead separation of  $\sim 1.9$ Å. In [3]2m, obtained<sup>5</sup> by telomerization of 1 with (CH<sub>3</sub>COS)<sub>2</sub>,

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(15) Obtained by Vincent Lynch.  $C_{12}H_{16}O_2$ , monoclinic  $P2_1/m$  (no. 11) a = 5.793 (2) Å, b = 8.690 (3) Å, c = 11.111 (2) Å,  $\beta = 96.13$  (1)°, V = 556.2 (3) Å<sup>3</sup>, D(calcd) = 1.15 g-cm<sup>-1</sup> for Z = 2,  $\mu(\text{Mo } K\alpha) = 0.7155$  cm<sup>-1</sup>. A total of 2735 reflections (1367 unique reflections,  $R_{\text{INT}} = 0.0226$ ) using the  $\omega$  scan technique with a scan range of 1° in  $\omega$  from  $4 < 2\theta < 50^\circ$ . Of these, 971 were considered observed  $[F_0 \ge 4(\sigma(F_0))]$ . The data were corrected for LP, absorption, and decay. The structure was solved by direct methods and refined by full-matrix least-squares procedures to a final R = 0.0680 and  $R_w = 0.0606$ . Collected on a Syntex P2<sub>1</sub> diffractometer at 163 K.

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Figure 2. The structure of methyl [2]staffane-3-carboxylate.<sup>14</sup>

the inter-ring distances are even shorter, 1.47 Å.5 Neighboring staffs are parallel and meshed in the crystal, with axes only 4.6 Å apart. This very efficient packing is undoubtedly responsible for the high melting points.

The salts of the acids [n]2b are surface active. In the concentration range  $c = 1.4 \times 10^{-2} - 3 \times 10^{-4}$  M, the surface tension<sup>16</sup> of an aqueous solution of the potassium salt of [3]2b follows  $\gamma$ =  $-17.7 \log c - 0.2 \, dyn/cm$  (107 Å<sup>2</sup> of surface area per molecule). Langmuir-Blodgett films have been prepared by using the Cd<sup>2+</sup> salt of [4]2b (45 Å<sup>2</sup>/molecule).<sup>18</sup>

The NMR spectra of the "staffs" clearly show each equivalent class of <sup>1</sup>H and <sup>13</sup>C nuclei up to n = 5. Large bridgeheadbridgehead coupling constants are attributed to transannular orbital interactions,<sup>19</sup> e.g., in [2]2i,  $^{7}J[^{31}P^{1}H] = 1.7$  Hz. The CP-MAS <sup>13</sup>C NMR spectrum of [poly]2a consists of a peak at  $\delta$  50.8 (bridge), a sharp peak at  $\delta$  40.3 (bridgehead), and weak end-group signals at  $\delta$  169.7 (carbonyl) and  $\delta$  27.8 (methine).

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## The Role of Oxygen in the Partial Oxidation of Methane over a Samarium Oxide Catalyst

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The reaction of methane with oxygen at high temperatures to form higher hydrocarbons such as ethane and ethylene was first reported by Ito et al.,1 who used a lithium-doped magnesium oxide catalyst and suggested that the reaction involved the formation of methyl radicals on Li<sup>+</sup>O<sup>-</sup> sites and their subsequent gas-phase dimerization. The reaction presents an intriguing mechanistic problem, particularly as it is now known to be catalyzed by a wide range of materials.<sup>2</sup> Samarium oxide appears to be one of the most active catalysts.<sup>3</sup> Details of the reaction mechanism are obscure at present, but it is obvious that the formation of C2 hydrocarbons at these high temperatures in the presence of oxygen

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